

Equilibrium structure of erbium-oxygen complexes in crystalline silicon

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The equilibrium structure of ErO_n ($n \leq 6$) complexes in crystalline silicon has been investigated by density-functional computations. Two different geometries have been considered, corresponding to the substitutional and tetrahedral interstitial site for erbium. All atomic coordinates have been optimized by Car-Parrinello molecular dynamics. The resulting structures have low symmetry, with E-O distances of ~ 2.35 Å. The substitutional site is the most stable one for $n \leq 2$, while the tetrahedral interstitial is favored for $n > 2$.

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The low luminescence efficiency of crystalline silicon represents a major roadblock in the increasing integration of electronic devices with optoelectronic components.¹ A promising route to overcome this limitation involves the incorporation of rare-earth centers, able to provide a large enhancement of the luminescence efficiency.^{2,3}

In the last few years, the attention has been focused on erbium doping, which gives rise to a sharp luminescence line at $\lambda = 1.54$ μm , due to the $I_{3/2} \rightarrow I_{15/2}$ transition in the $4f^{11}$ shell of Er^{3+} . From the application point of view, this transition presents two crucial features: it is nearly independent of the local environment, since it occurs in electronic states strongly localized around the Er^{3+} core; it matches very closely to the optimal transmission frequency of silicon dioxide waveguides. Extensive experimental investigations (reviewed in Ref. 2 and Ref. 3) have highlighted the role of co-dopants in the preparation and stabilization of photoluminescent samples: highly electronegative elements (O, F, and, to a lesser extent, also N and C) increase the optical activity of the Er centers, decrease thermal quenching of the luminescence, and enhance the equilibrium solubility of Er well above the limit for pure silicon. The optimization of these effects requires the precise determination of the structure of Er centers, as well as its dependence on the concentration of co-dopants and on sample preparation. Unfortunately, the available experimental information is far from being complete and unambiguous, since low Er solubility and disorder prevent the application of the most powerful structural determination tools. Moreover, these systems are usually produced by ion implantation followed by annealing, and kinetic effects play a major role in determining the sample quality and structure. Different experiments, however, agree on the fact that in pure Si the Er-Si first coordination shell has a radius of 3 Å, while in the presence of oxygen Er is coordinated by 4–6 O atoms, with an Er-O distance of ~ 2.27 Å.⁴

Theoretical and computational methods could play a major role in elucidating structural features for this system. A pioneering application of density-functional (DF) methods⁵ to the determination of the Er equilibrium position in crystalline Si was reported in Ref. 6. Unfortunately, this first investigation was not followed by more extensive studies, partly because of the widespread skepticism on the reliability

of popular DF approximations in dealing with f -electron systems, and partly because of the complexity and cost of these computations.

Although the limitations of local and semilocal DF approximations in describing the electronic structure of f -electron systems are well documented,⁷ a growing number of computations has shown that structural properties can be described by these methods at an acceptable (although far from excellent) level of accuracy.⁸

We applied a gradient corrected DF approximation to the investigation of structural properties of Er and Er-O_n (n up to 6) complexes in silicon. Our study extends that of Ref. 6, not only because we consider the Er-oxygen complexes in addition to the isolated Er defect, but because we include explicitly the f electrons in our computation, we consider larger systems, and we optimize the atomic positions without introducing any symmetry constraint. The results identify the different equilibrium structures of the system as a function of oxygen concentration, and provide useful insight for the interpretation of the experimental data.

The computation of the DF total energy as a function of the atomic coordinates is performed using a recent gradient corrected approximation for the exchange and correlation energy.⁹ This same approximation provided excellent results for silica,¹⁰ as well as for a variety of covalent and ionic systems,¹¹ and therefore we expect that it will describe reliably both the Si-O bonds, and the (mainly Coulombic) interactions of Er.

Only valence electrons are included in the computation, and their interaction with the atomic cores is described by soft, norm-conserving pseudopotentials.¹² All computations involve a single Er atom and n oxygens ($n = 0, \dots, 6$) within a simple cubic supercell containing 64 Si atoms for the interstitial complexes, and 63 Si atoms for the substitutional case. Periodic boundary conditions are applied. The comparison of total energies is carried out by adding to the substitutional case (63 Si atoms) the total energy of the missing Si atom, considered in equilibrium with a perfect silicon crystal.

The Brillouin zone of the supercell is sampled at the Γ -point only,¹³ and the Kohn-Sham orbitals are expanded on a basis of plane waves with a kinetic-energy cutoff of 120 Ry, with a corresponding cutoff for the electron density of 480 Ry. Convergence has been tested by performing compu-

tations for a few selected samples using 140 Ry. Energy differences are reproduced to better than 0.05 eV, and bond distances change less than 0.01 Å.

For each sample, the total energy is minimized with respect to the atomic coordinates, using quenched molecular dynamics in the Car-Parrinello implementation.¹⁴

The lattice constant a_0 of each (ErO_n) -Si supercell is determined by minimizing the energy. An isolated impurity, of course, does not change the lattice periodicity, and an equally justifiable choice would be of keeping constant the lattice parameter of the supercell at the crystal silicon value. Our choice of optimizing the volume implies that our results are strictly valid for systems at the doping concentration of 1 Er/64 Si atoms. However, the volume relaxation is small, and we think that the results of the present computation are valid for the entire range of low Er and O concentrations relevant for applications.

Previous computations for Er in pure silicon⁶ adopted a very simple pseudopotential, including only the 6s electrons in the valence charge. Different oxidation states (+2 and +3) were accounted for by using ionized configurations in the pseudopotential generation, and total energies computed with different pseudopotentials were compared by including an empirical correction. The drastic improvements in computer performances and numerical implementations of the last ten years now allow us to include the 4f electrons in the valence charge. These electrons do not play a major *direct* role in the bonding of Er. Nevertheless, their inclusion in the valence charge allows the system to adopt the most favorable oxidation state, and, more importantly, it provides an unbiased description of the short-range screening of the Er cation.

Test computations for the Er atom in the ground state and in the lowest energy excited states have shown that the energy and radius of the 6p shell (that is unoccupied in the atomic ground state, but, together with the 5d shell, plays a role in the formation of Er-O bonds) is very sensitive to the details of the pseudopotential generation. The uncertainty on the most appropriate reference state was not satisfactorily removed even by using the scheme proposed in Ref. 15 to deal with 4f atoms. The detailed analysis of the Er atomic orbitals has shown that the problem arises because of large relaxations in the underlying 5p state upon changing the 4f population, that, in turn, are due to a substantial overlap of the 4f and 5p shells. For these reasons, we included also the 5p shell in the valence charge. The 5s level is 1Ry lower in energy than the 5p, and is considered a core state. To account for its spatial overlap with both 5p and the 4f, non-linear core corrections¹⁷ are included. With this last addition, the pseudopotential is able to reproduce fairly well the all electron results for the energy and spatial localization of the lowest energy excited states of the Er atom. Quantitative discrepancies are still present, underlining the difficulty of building fully reliable pseudopotential models for *f*-electron atoms.¹⁶ The pseudopotentials for O and Si have been produced following standard and extensively tested procedures, and have already been used in several other computations. The method has been tested by computing the total energy as a function of volume for Er_2O_3 in the structures identified in Ref. 18. The results show that the computation overestimates

the lattice constant by 2.8%,¹⁶ an error that can be considered acceptable given the complexity of the system.

The combined effect of Er, O, and Si ionic bonding, of deviations from the natural stoichiometry of these elements, and of the relatively small simulation supercell raise the problem of the most appropriate charge state for our samples. The results reported below have been obtained with neutral samples. Energy and structural differences for different choices of the total charge have been computed in a few cases, and found to be small.

The Er atom has 12 electrons in the incomplete 4f shell, and the population of this level decreases to 11e, in the +3 oxidation state. The Er ion, therefore, has a net spin moment. However, our computations have been done within the spin restricted approximation, assuming that the strong localization of the 4f shell limits the influence of spin on bonding. This assumption has been tested by two explicit computations for an isolated Er and for the ErO complex in silicon, again showing only minor changes with respect to the spin restricted computation.

The total energy and structure of ErO_n complexes in crystalline silicon has been determined by relaxing initial configurations suggested by experimental data and by previous computational studies.⁶ The local stability of the resulting configurations has been tested by simulated annealing cycles reaching a temperature $T \sim 1000$ K, and lasting a few ps.

For the isolated Er impurity, we considered the substitutional configuration (T_s), as well as the interstitial sites of tetrahedral (T_i) and hexagonal (H_i) symmetry. The substitutional site (T_s) turns out to be the most stable one; the energy of the T_i and H_i sites being 0.5 eV and 0.7 eV higher, respectively. The equilibrium position of Er is displaced with respect to the ideal one by 0.70 Å, 0.30 Å, and 0.31 Å for the T_s , T_i , and H_i cases, respectively. Also the silicon sublattice appears to be locally deformed, as apparent in Fig. 1(a), illustrating the relaxed geometry of the T_s case. In the first coordination shell, the displacements of the Si atoms from their ideal lattice position are comparable to those computed for Er, i.e., of the order of 0.5 Å. In all cases, deformations are consistent with a repulsive interaction between Er and Si at the distances imposed by the Si lattice. This size mismatch is probably the reason of the low solubility of Er in Si, and could also explain the relative energy of the T_s , T_i , and H_i sites, since the Er nearest-neighbor (NN) distances ($d[\text{Er}-\text{Si}] = 2.91$ Å, 2.60 Å, and 2.55 Å, for the T_s , T_i , and H_i sites, respectively) decrease in parallel with the decreasing stability of these geometries. We notice that the NN Er-Si distance in the T_s site is close to the experimental estimates.

Our results contrast with those of Ref. 6, predicting a tetrahedral interstitial ground state. We do reproduce the results of Ref. 6 if we adopt the same reduced pseudopotential, and therefore we attribute the disagreement to the different choice of the pseudopotential.

Starting from the relaxed configurations for the isolated impurity, we progressively added oxygen atoms in the vicinity of Er, selecting initial oxygen positions that avoided close contacts with other atoms, but that were otherwise unbiased. For each n and for each Er site, several initial configurations

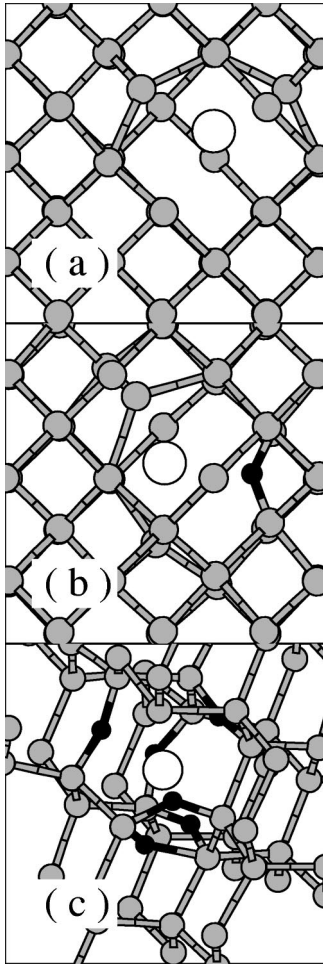


FIG. 1. Equilibrium geometries for selected ErO_n centers in Si: (a) $n=0$, T_s site; (b) $n=1$, T_s site; (c) $n=6$, T_i site. Er is represented by the large white circle, oxygen by black circles, while the gray circles are Si atoms.

have been considered. The sequence originated from the hexagonal interstitial site consistently displayed higher energies than in the other two cases, and therefore we did not continue it beyond two O neighbors. We focused instead on the other two sites, that have been investigated for complexes with up to six oxygen atoms.

The energy difference between the T_s and T_i sites is reported in Fig. 2 as a function of oxygen coordination. It is apparent that the slight energy advantage found for the isolated Er in the T_s site vanishes for $n=2$, and at higher n 's the T_i site is energetically favored with respect to T_s .

In both sites, the progressive inclusion of oxygen gives rise to large local distortion of the Si lattice and to disorder, as can be seen in Fig. 1(b),(c), and inferred from Fig. 3, reporting the O and Si coordination number as a function of distance from Er. This last figure shows that the Si lattice deformation extends over a wider range in the T_s case, while it is confined to the nearest-neighbor shell for T_i . This difference could be at the origin of the observed energy trends.

In all cases, the local coordination of Er does not have any apparent symmetry, apart from the fact that, for the highest n 's, O atoms tend to form an approximately isotropic shell.

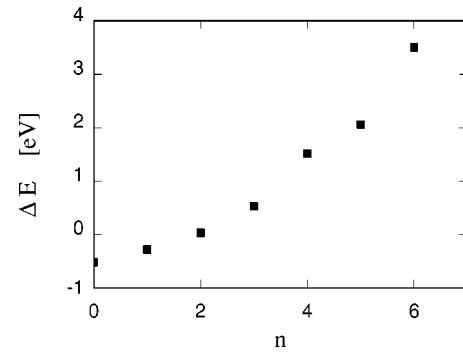


FIG. 2. Total energy difference $\Delta E = E_{tot}[T_s] - E_{tot}[T_i]$ between the T_s and the T_i sites as a function of oxygen coordination n .

For $n > 2$ the Er-O distances display also significant fluctuations, ranging from 2.19 Å to 2.42 Å (average distance 2.33 Å) in the case of ErO_6 at T_s , and from 2.25 Å to 2.45 Å (average distance 2.35 Å) for the T_i site. Both the average distance and the distance fluctuations increase slightly but monotonically with increasing n , pointing to a saturation of the Er-O effective attraction with increasing O coordination.

At the oxygen concentration corresponding to experiments ($n \geq 5$), the computed distances overestimate the experimental Er-O separations by almost 4%. Part of the discrepancy simply reflects the overestimation of the lattice constant of crystalline Er_2O_3 (see above). The remaining discrepancy ($\sim 1\%$) does not have an obvious explanation.

In a few cases, simulated annealing runs did provide qualitatively different geometries, with average Er-O distances (2.28 Å) shorter than those reported above, and closer to the experimental data. The energy of these struc-

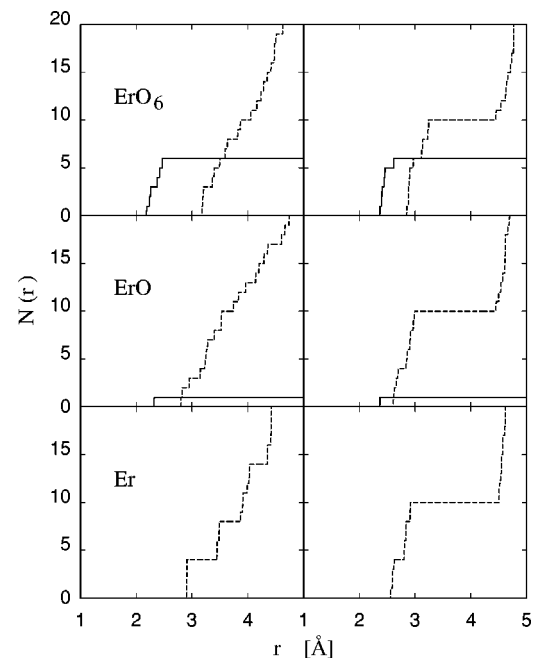


FIG. 3. Running coordination number $N(r)$ for Er in the T_s (left) and T_i sites (right). Full line: oxygen atoms. Dash line: Si atoms.

tures, however, was significantly higher (by at least 0.8 eV) than that of the geometries described above.

In conclusion, the equilibrium geometry of ErO_n ($0 \leq n \leq 6$) complexes in crystalline silicon has been investigated by DF computations. Structures with Er in the T_s , T_i , and H_i sites have been considered as starting point for extensive geometry optimizations. At low oxygen concentration ($n \leq 2$) the T_s site provides the most stable configuration. At higher oxygen content, the T_i site becomes the most stable site. The H_i site appears to be higher in energy than either the T_s and T_i cases. In all cases, the local O coordination of Er displays low spatial symmetry.

Because of the strong directionality and stiffness of the Si and O covalent bonds, we do not expect that our limited annealing runs are able to overcome significant energy barriers, progressing much beyond the local minimum in the potential energy surface closest to the starting point. Nevertheless, our strategy avoids the most unstable configurations, and the structures we find should be representative of those present in experimental samples.

Comparison of our results with experimental data shows that our method overestimates Er-O distances by 3% (for Er_2O_3) to 4% (for the highest coordinated complexes). Similar discrepancies are not uncommon for DF computations involving rare-earth atoms. Further computations are in progress to clarify whether the discrepancy is due to the pseudopotentials or to the exchange-correlation approximation.

The comparison is less stringent for what concerns the type (either T_s or T_i) of the equilibrium complexes, since different experiments give contradictory results, suggesting that kinetic effects are crucial not only for the short annealing runs allowed by simulation, but also on the time scale of experiments. The sizable energy differences between the T_s and T_i sites, however, enhance our confidence in the computational identification of the *equilibrium* geometry, especially at the highest O concentrations, that are the most relevant for experiments and applications. We underline that these energy differences are computed for systems with very similar chemical character, for which errors due to the exchange-correlation approximation or to the pseudopotential are expected to be nearly equal.

The inherent limitations of the DF method prevent a direct discussion of photoluminescence efficiency for this system. Nevertheless, our computations provide indirect information relevant for photoluminescence. For instance, the apparent distortion in the local Er environment, that becomes more important with increasing O concentration, implies that the radiative de-excitation of the $I_{3/2} \rightarrow I_{15/2}$ transition is progressively less affected by symmetry restrictions. The real value of our computations, however, is to provide additional data to tune microscopic models for the structure, stability, and optical properties of this system.

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